

DIRECT CALCULATION OF CONTRIBUTIONS TO THE SECOND ORDER ENERGY
OF HELIUM *

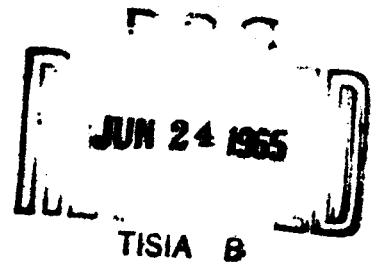
by

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ABSTRACT

The first order perturbed wave function of helium is written as a sum of terms due to various electron excitations. The portion of the first order wave function due to one-electron excitations has been determined by several investigators. The portion due to two-electron excitations with one of the electrons excited to the 2s orbital is determined exactly by solving a differential equation and evaluating an integral. The contributions of these functions to the second order energy are computed and found to be in exact agreement with the energies determined by direct summation of the spectral expansion.



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1. Introduction

In recent years there have been many attempts to solve fundamental quantum mechanical problems by applications of perturbation theory. For many one-electron problems explicit solutions of the perturbation equations have been obtained. However, such explicit solutions are impossible when the perturbation involves the two-particle electron repulsion potential $1/r_{12}$. To overcome this difficulty a perturbation-variation method has been used extensively.¹ However, it is sometimes possible to obtain differential equations, for certain well defined parts of the perturbed wave function, which can be solved explicitly.

As an example, we consider the ground state energy of the helium atom. Treating $1/r_{12}$ as a perturbation, the first order wave function and the second order energy are separated into contributions due to various electronic excitations. The contributions due to one-electron excitations have been calculated by several investigators.² We calculate the contribution due to two-electron excitations with one

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1. For example see the review article by J. O. Hirschfelder, W. Byers Brown and S. T. Epstein, in "Advances in Quantum Chemistry" (edited by P. O. Lowdin, Academic Press, New York, 1964), p. 225 et seq.
 2. (a) M. Cohen and A. Dalgarno, Proc. Phys. Soc. 77, 165 (1961).
(b) J. Linderberg, Phys. Rev., 121, 816 (1961).
(c) C. S. Sharma, Proc. Phys. Soc. 80, 839 (1962).
(d) C. S. Sharma and C. A. Coulson, Proc. Phys. Soc., 80, 81 (1962).
(e) M. Cohen, Proc. Phys. Soc. 82, 778 (1963).
(f) D. Layzer; Z. Horak, M. N. Lewis and D. P. Thompson, Ann. Phys. 29, 101 (1964).

of the electrons excited to the 2s orbital. The results are in complete agreement with the values Scherr³ obtained by direct summation of the spectral expansion of the second order energy.

2. Theory

The Hamiltonian for a two-electron atom is taken to be

$$H = Z^2 \left[-\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z r_{12}} \right] \quad (1)$$

where the units of length and energy are a_0/Z and e^2/a_0 respectively.

This Hamiltonian can be separated into $H/Z^2 = H_0 + V/Z$ where

$$H_0 = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} \quad , \quad (2)$$

and

$$V = \frac{1}{r_{12}} \quad (3)$$

Treating V as a perturbation and taking as the zeroth order wave function

$$\Psi^{(0)} = \psi_{1s}^{(1)} \psi_{1s}^{(2)} = \pi^{-1} \exp(-r_1 - r_2) \quad (4)$$

we obtain a series in powers of $1/Z$ for the ground state energy

3. C. W. Scherr, J. Chem. Phys. 33, 317 (1960).

of the two-electron atom,

$$\begin{aligned} E &= Z^2 E^{(0)} + Z E^{(1)} + E^{(2)} + Z^{-1} E^{(3)} + \dots \\ &= -Z^2 + \frac{5}{8} Z + E^{(2)} + \dots \end{aligned} \quad (5)$$

The first order Rayleigh-Schrödinger correction to the zeroth order wave function, $\Psi^{(1)}$, due to the perturbation V , can be expanded in the eigenfunctions of H_0 ,

$$\Psi^{(1)} = \sum_j \sum'_k \frac{V_{j,k;1s,1s}}{2E_{1s} - E_j - E_k} \phi_{j,k} \quad (6)$$

In Eq. (6) the subscripts j and k denote the hydrogenic orbitals, i.e. $j, k = 1s, 2s, 2p, \dots$,

$$\phi_{j,k} = N_{j,k} [\Psi_{j(1)} \Psi_{k(2)} + \Psi_{j(2)} \Psi_{k(1)}] \quad (7)$$

where $N_{j,k}$ is the appropriate normalization factor, and

$$V_{j,k;l,m} = \langle \phi_{j,k}, V \phi_{l,m} \rangle \quad (8)$$

The primed sigma in Eq. (6) indicates that the term with $j = k = 1s$ is excluded from the expansion and that each pair, j and k , is counted only once.

The double sum in Eq. (6) can be written as

$$\begin{aligned}
\Psi^{(1)} &= \sum_{R \neq 1s} \frac{V_{1s,R;1s,1s}}{E_{1s} - E_R} \phi_{1s,R} + \sum_{R \neq 1s} \frac{V_{2s,R;1s,1s}}{2E_{1s} - E_{2s} - E_R} \phi_{2s,R} \\
&\quad + \sum_{R \neq 1s, 2s} \frac{V_{2p,R;1s,1s}}{2E_{1s} - E_{2p} - E_R} \phi_{2p,R} + \dots \\
\Psi^{(1)} &= \Psi_{1s}^{(1)} + \Psi_{2s}^{(1)} + \Psi_{2p}^{(1)} + \dots
\end{aligned} \tag{9}$$

Here $\Psi_{1s}^{(1)}$ represents the contribution of one-electron excitations to the first order wave function, $\Psi_{2s}^{(1)}$ the contribution of two-electron excitations with one electron in the 2s orbital, and so on.

The second order correction to the zeroth order energy, $E^{(2)}$, due to the perturbation V , is given by

$$\begin{aligned}
E^{(2)} &= \langle \Psi^{(0)}, V \Psi^{(1)} \rangle \\
&= \langle \Psi^{(0)}, V \Psi_{1s}^{(1)} \rangle + \langle \Psi^{(0)}, V \Psi_{2s}^{(1)} \rangle + \dots \\
&= E_{1s}^{(2)} + E_{2s}^{(2)} + \dots
\end{aligned} \tag{10}$$

Therefore, to calculate the contributions to the second order energy from various electronic excitations it is only necessary to find explicit expressions for $\Psi_j^{(1)}$. This can be done, as will be illustrated in the next two sections of this paper, by an extension of a method which Schwartz⁴ used to calculate the first order correction to the one-electron density of the helium atom.

3. Calculation of $\Psi_{1s}^{(1)}$ and $E_{1s}^{(2)}$

A perturbation treatment of the Hartree-Fock approximation of the ground state energy of helium has been carried out by several investigators². It is well known that $\Psi_{1s}^{(1)} = \Psi_{HF}^{(1)}$ and

4. C. Schwartz, Ann. Phys. 2, 156 (1959). See also G. G. Hall, L. L. Jones and D. Rees, Proc. Roy. Soc. 283, 194 (1965).

$$\epsilon_{1s}^{(2)} = \epsilon_{HF}^{(2)} .$$

The first order wave function, $\Psi^{(1)}$, satisfies the differential equation

$$(H_0 - \epsilon^{(0)}) \Psi^{(1)} = (\epsilon^{(1)} - V) \Psi^{(0)} . \quad (11)$$

If we require the total wave function to be real and normalized through first order, then $\Psi^{(1)}$ also satisfies the orthogonality condition

$$\langle \Psi^{(0)}, \Psi^{(1)} \rangle = 0 . \quad (12)$$

Equations (9) and (11) give

$$(2\epsilon_{1s} - H_0)(\Psi_{1s}^{(1)} + \Psi_{2s}^{(1)} + \dots) = (V - \epsilon^{(1)}) \Psi^{(0)} \quad (13)$$

Multiplying by $\Psi_{1s}^{(2)}$ and integrating over the configuration space of electron 2, Eq. (13) gives

$$(\epsilon_{1s} - h_1) \int \Psi_{1s}^{(2)} \Psi_{1s}^{(1)} d\tau_2 = (V_{1s;1s}^{(1)} - \epsilon^{(1)}) \Psi_{1s}^{(1)}, \quad (14)$$

where

$$h_1 = -\frac{1}{2} \nabla_1^2 - \frac{1}{r_1} , \quad (15)$$

and

$$V_{i,j} = \langle \Psi_{i(2)}, V \Psi_{j(2)} \rangle \quad (16)$$

Defining

$$\chi_{is}^{(1)} = \int \Psi_{is(2)} \Psi_{is}^{(1)} d\tau_2, \quad (17)$$

and evaluating $V_{is, is}^{(1)}$, Eq. (14) yields

$$(\epsilon_{is} - h_i) \chi_{is}^{(1)} = \left\{ \frac{1}{r_i} [1 - (1+r_i) \exp(-2r_i)] - \frac{5}{8} \right\} \Psi_{is}^{(1)}. \quad (18)$$

It can be shown from Eqs. (9), (14) and (17) that

$$\Psi_{is}^{(1)} = \chi_{is}^{(1)} \Psi_{is(2)} + \chi_{is(2)} \Psi_{is}^{(1)}. \quad (19)$$

Therefore to obtain an explicit expression for $\Psi_{is}^{(1)}$ it is necessary to solve Eq. (18).

Equation (18) is easily integrated by quadrature, and the solution satisfying the orthogonality condition Eq. (12) is⁴

$$\chi_{is}^{(1)} = \left[-\frac{23}{32} - \frac{3}{8} \gamma - \frac{3}{8} \ln r_i + \frac{5}{8} r_i - \frac{1}{4} \exp(-2r_i) + \frac{3}{16r_i} [1 - \exp(-2r_i)] + \frac{3}{8} E_i(-2r_i) \right] \quad (20)$$

where γ is Euler's constant.

From Eq. (10) the contribution of one-electron excitation to the second order energy is

$$E_{1s}^{(2)} = \frac{1}{32} \left(9 \ln \frac{3}{4} - \frac{26}{27} \right) = -0.1110032. \quad (21)$$

The second order energy has been evaluated by the perturbation-variation method⁵: $E^{(2)} = -0.1576664$. An expansion of the first order wave function in Legendre functions, $P_l(\cos \theta_2)$, leads to an expansion of the second order energy, $E^{(2)} = \sum_l E_l^{(2)}$. The quantity $E_0^{(2)}$ is customarily referred to as the radial limit of $E^{(2)}$, and has the value⁶ $E_0^{(2)} = -0.12533198$. Therefore $E_{1s}^{(2)}$ gives 70.4 per cent of $E^{(2)}$ and 88.6 per cent of $E_0^{(2)}$.

4. Calculation of $\Psi_{2s}^{(1)}$ and $E_{2s}^{(2)}$

Multiplying Eq. (13) by $\Psi_{2s}^{(2)}$ and integrating over the configuration space of electron 2 gives

$$(2E_{1s} - E_{2s} - h_1) \int \Psi_{2s}^{(2)} [\Psi_{1s}^{(1)} + \Psi_{2s}^{(1)}] d\tau_2 = V_{1s;2s}^{(1)} \Psi_{1s}^{(1)}. \quad (22)$$

Defining

$$\chi_{2s}^{(1)} = \int \Psi_{2s}^{(2)} \Psi_{2s}^{(1)} d\tau_2, \quad (23)$$

Eq. (22) yields

5. C. W. Scherr and R. E. Knight, Rev. Mod. Phys. 35, 436 (1963).
See also E. A. Hylleraas and J. Midtdal, Phys. Rev. 103, 829 (1956); 109, 1013 (1958).
6. C. W. Scherr and R. E. Knight, J. Chem. Phys. 40, 1777 (1964).
See also C. Schwartz, Phys. Rev. 126, 1015 (1962).

$$(2\epsilon_{1s} - \epsilon_{2s} - h_1) \chi_{2s}^{(1)} = \frac{4(2)^{1/2}}{27} \left[\left(1 + \frac{3}{2}r_1\right) \exp\left(-\frac{3}{2}r_1\right) - \frac{1024}{2401} \right] \psi_{1s}^{(1)} \quad (24)$$

Multiplying Eq. (24) by $\psi_{1s}^{(1)}$ and integrating over the configuration space of electron 1 yields the condition

$$\langle \psi_{1s}^{(1)}, \chi_{2s}^{(1)} \rangle = 0 \quad (25)$$

From Eqs. (9) and (23) it can be shown that

$$\begin{aligned} \Psi_{2s}^{(1)} &= \chi_{2s}^{(1)} \psi_{2s}^{(2)} + \chi_{2s}^{(2)} \psi_{2s}^{(1)} \\ &\quad - \frac{V_{2s,2s;1s,1s}}{2\epsilon_{1s} - 2\epsilon_{2s}} \psi_{2s}^{(1)} \psi_{2s}^{(2)} \end{aligned} \quad (26)$$

While Eq. (24) cannot be integrated easily by quadrature (see appendix), a solution containing an infinite series can easily be obtained and may be written as

$$\chi_{2s}^{(1)} = \left(\sum_{m=0}^{\infty} A_m r_1^m \exp\left(-\frac{3}{2}r_1\right) + \frac{4(2)^{1/2}}{3} V_{1s,2s;1s,1s} \right) \psi_{1s}^{(1)} \quad (27)$$

where

$$A_1 = \frac{3}{2} A_0 \quad (28)$$

$$A_2 = \frac{5}{4} A_0 + \frac{4(2)^{1/2}}{81} \quad (29)$$

$$A_3 = \frac{19}{24} A_0 + \frac{22(2)^{1/2}}{243} \quad (30)$$

and

$$A_m = \frac{(5m-2)A_{m-1} - \frac{9}{2}A_{m-2}}{m(m+1)}, \text{ for } m \geq 4. \quad (31)$$

Substituting Eq. (27) into Eq. (25) yields

$$\sum_{n=0}^{\infty} A_n \left(\frac{2}{7}\right)^n (n+2)! = -\frac{1024(2)^{1/2}}{567} \quad (32)$$

This equation can be rearranged to give

$$A_0 = - \left[\frac{1024(2)^{1/2}}{567} + \sum_{n=0}^{\infty} C_n \left(\frac{2}{7}\right)^n (n+2)! \right] \times \left[\sum_{n=0}^{\infty} B_n \left(\frac{2}{7}\right)^n (n+2)! \right]^{-1} \quad (33)$$

where

$$\begin{aligned} B_0 &= 1 & ; & & C_0 &= 0 \\ B_1 &= \frac{3}{2} & ; & & C_1 &= 0 \\ B_2 &= \frac{5}{4} & ; & & C_2 &= \frac{4(2)^{1/2}}{81} \\ B_3 &= \frac{19}{24} & ; & & C_3 &= \frac{22(2)^{1/2}}{243} \end{aligned}$$

and B_m and C_m satisfy the recursion relation Eq. (31). The ratio of the two divergent series in Eq. (33) can be evaluated numerically to give $A_0 = 0.15093374$.

From Eqs. (10) and (26) we have

$$\begin{aligned}
E_{25}^{(2)} &= 2 \langle \psi_{15}^{(1)} \psi_{15}^{(2)}, V \chi_{25}^{(1)} \psi_{25}^{(2)} \rangle - \frac{(V_{25,25;15,15})^2}{2E_{15} - 2E_{25}} \\
&= \frac{2^{29}}{3^7 \times 7^8} + \frac{2^4 (2)^{1/2}}{3^3 \times 5^4} \sum_{n=0}^{\infty} A_n \frac{(3n+19)(n+2)!}{5^n} + \frac{2^{10}}{3^{13}} \\
&= -0.004292603
\end{aligned} \tag{34}$$

This is in agreement with the value obtained by Scherr.^{3,7} It gives 2.7 per cent of $E^{(2)}$ and 3.4 per cent of $E_0^{(2)}$. The sum of $E_{15}^{(2)}$ and $E_{25}^{(2)}$ gives 73.1 per cent of the second order energy and 92.0 per cent of the radial limit. This result indicates that the series expansion of the second order energy converges slowly.

The method used in this report can be extended to other terms in the expansion of the first order wave function and the second order energy. However, the differential equations involved in the treatment become progressively more difficult to solve.

Acknowledgement

The authors wish to thank W. Byers Brown for many helpful discussions.

7. This result may also be obtained from Eqs. (4.1b) and (4.9) of ref. 2(f).

Appendix

Equation (24) can be written as

$$(h + \epsilon) \chi(r) = R(r) \quad (\text{A.1})$$

where h is the one-electron Hamiltonian. A general solution of this equation can be obtained as a quadrature involving solutions of the homogeneous equation. This is most easily done by making the following transformation

$$\chi = (\epsilon)^{1/2} r \quad (\text{A.2})$$

and

$$\chi(r) = G(x) \exp(-\frac{x}{2}) \quad (\text{A.3})$$

Equation (A.1) now becomes

$$x \frac{d^2}{dx^2} G(x) + (\beta - x) \frac{d}{dx} G(x) - \alpha G(x) = S(x) \quad (\text{A.4})$$

where

$$\alpha = 1 - (2\epsilon)^{1/2} \quad ; \quad \beta = 2$$

$$S(x) = -\frac{x}{4\epsilon} R\left(\frac{x}{(2\epsilon)^{1/2}}\right) \exp\left(\frac{x}{2}\right)$$

The homogeneous equation

$$x \frac{d^2}{dx^2} \tilde{G}(x) + (\beta - x) \frac{d}{dx} \tilde{G}(x) - \alpha \tilde{G}(x) = 0 \quad (\text{A.5})$$

is the confluent hypergeometric differential equation with the solutions:⁸

$$M(\alpha, \beta, x) = \sum_{m=0}^{\infty} \frac{(\alpha)_m x^m}{(\beta)_m m!} \quad (\text{A.6})$$

where

$$(\alpha)_m = \alpha(\alpha+1) \cdots (\alpha+m-1) ; (\alpha)_0 = 1$$

and

$$U(\alpha, \beta, x) = \frac{(-1)^\beta}{(\beta-1)! \Gamma(\alpha-\beta+1)} \left[M(\alpha, \beta, x) \ln x + \sum_{k=0}^{\infty} \frac{(\alpha)_k x^k}{(\beta)_k k!} \left\{ \Psi(\alpha+k) - \Psi(1+k) - \Psi(\beta+k) \right\} \right] \\ + \frac{(\beta-2)!}{\Gamma(\alpha)} \sum_{k=0}^{\beta-2} \frac{(\alpha-\beta+1)_k x^{k-\beta+1}}{(2-\beta)_k k!} \quad (\text{A.7})$$

8. See for example; Lucy J. Slater, "Handbook of Mathematical Functions". (edited by M. Abramowitz and Irene A. Stegun, National Bureau of Standards, Washington, 1964), Ch. 13.

for $\beta = 1, 2, \dots$ and $\psi(\alpha) = \Gamma'(\alpha)/\Gamma(\alpha)$ where $\Gamma(\alpha)$ denotes the gamma function.

These solutions have the following asymptotic behavior:

$$M(\alpha, \beta, x) \sim e^x, \quad x \rightarrow \infty$$

$$U(\alpha, \beta, x) \sim x^{-\alpha} + O(x^{-\alpha-1}), \quad x \rightarrow \infty$$

$$M(\alpha, \beta, x) \sim 1 + \frac{\alpha}{\beta} x, \quad x \rightarrow 0$$

$$U(\alpha, \beta, x) \sim \frac{\Gamma(\beta-1)}{\Gamma(\alpha)} x^{1-\beta} + O(\ln x), \quad x \rightarrow 0, \text{ for } \beta=2.$$

The Wronskian of $M(\alpha, \beta, x)$ and $U(\alpha, \beta, x)$ is

$$W = -\frac{\Gamma(\beta)}{\Gamma(\alpha)} x^{-\beta} e^x \quad (\text{A.8})$$

The general solution of Eq. (A.4) can then be written as

$$G(x) = \frac{\Gamma(\alpha)}{\Gamma(\beta)} \left[M(\alpha, \beta, x) \left\{ \int U(\alpha, \beta, y) S(y) y^{\beta-1} \exp(-y) dy + C_1 \right\} - U(\alpha, \beta, x) \left\{ \int M(\alpha, \beta, y) S(y) y^{\beta-1} \exp(-y) dy + C_2 \right\} \right]. \quad (\text{A.9})$$

where C_1 and C_2 are arbitrary constants that can be chosen to satisfy the boundary conditions. However, the integrals in Eq. (A.9) give rise to double infinite sums in the solution of the inhomogeneous equation. Therefore, we have obtained a power series solution for Eq. (24).